Selenium-Containing Heterocycles from Isoselenocyanates: Synthesis of 1*H*-5-Selena-1,3,6-triazaaceanthrylene Derivatives

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The reaction of aryl isoselenocyanates **8** with methyl 3-amino-4-chloro-1-ethylpyrrolo[3,2-*c*]quinoline-2-carboxylate (**6**) in boiling pyridine leads to tetracyclic selenaheterocycles of type **9** in high yield (*Scheme 3*). A reaction mechanism *via* an intermediate selenoureido derivative **A** and cyclization *via* nucleophilic substitution of Cl by Se is proposed (*Schemes 3* and *5*). The reaction of **6** with 4-bromophenyl isothiocyanate yields the analogous thiaheterocycle **12** (*Scheme 4*). The molecular structures of **9c** and **12** have been established by X-ray crystallography.

1. Introduction. – The current interest in the chemistry of Se-containing compounds is well-documented (*cf.* [1–4] and refs. cit. in [5]). A series of recent papers deals with biological activities and the pharmaceutical potential of Se compounds (*e.g.*, [6–10]). For example, some organo-selenium compounds are active as insecticides and microbicides [11], as prooxidants [12], and antimycobacterial agents [13]. Recently, *Koketsu et al.* published some novel syntheses of selenaheterocycles [13–15].

Within our own research project, we have used aroyl isoselenocyanates **1a** and *N*-phenylbenzimidoyl isoselenocyanates **1b** as conveniently accessible, cheap, and safe Se reagents for the preparation of 1,2,3-selenadiazoles **2** [16] and 1,3-selenazole derivatives **3** [17], respectively (*Scheme 1*). In the case of **1c**, treatment with amines led to 6*H*-[5,1,3]benzoselenadiazocines **4** [18], whereas the base-catalyzed cyclization of **1d** yielded bis(2,4-diarylimidazol-5-yl) diselenides **5** [5].

Although the chemistry of Se-containing compounds is often similar to that of the corresponding S analogues, some significant differences are also known, and because of the toxicity and instability of many Se compounds, the synthesis of Se heterocycles is much less developed. Therefore, new approaches by using more stable, less toxic, and easily accessible Se reagents are of high interest. For this reason, we have investigated reactions of aryl isoselenocyanates as starting materials for the preparation of selenaheterocycles.

In the present paper, we report the results of the reaction of aryl isoselenocyanates with methyl 3-amino-4-chloro-1-ethylpyrrolo[3,2-*c*]quinoline-2-carboxylate (**6**). The latter was used recently by *Mekheimer* to prepare fused tri- and tetracyclic quinoline derivatives [19]. Among several transformations, he described the reaction with phenyl and allyl isothiocyanate, which gave – according to his interpretation – the corresponding 5-substituted methyl 1-ethyl-4-thioxo-3(4*H*)-1,3,5,6-tetraazaaceanthrylene-2-carboxylate **7** (*Scheme 2*).

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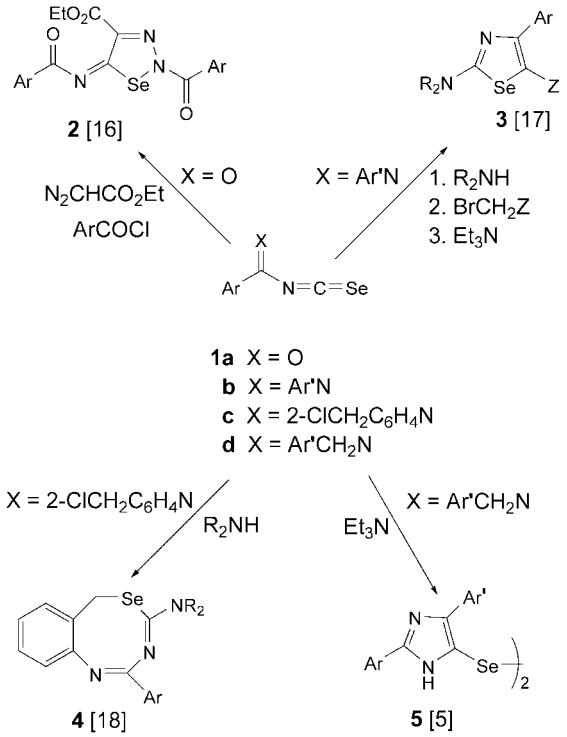
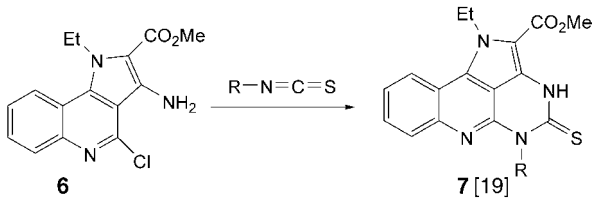
[1]) Part of the planned Ph.D. thesis of *P. K. A.*, Universität Zürich.

Scheme 1

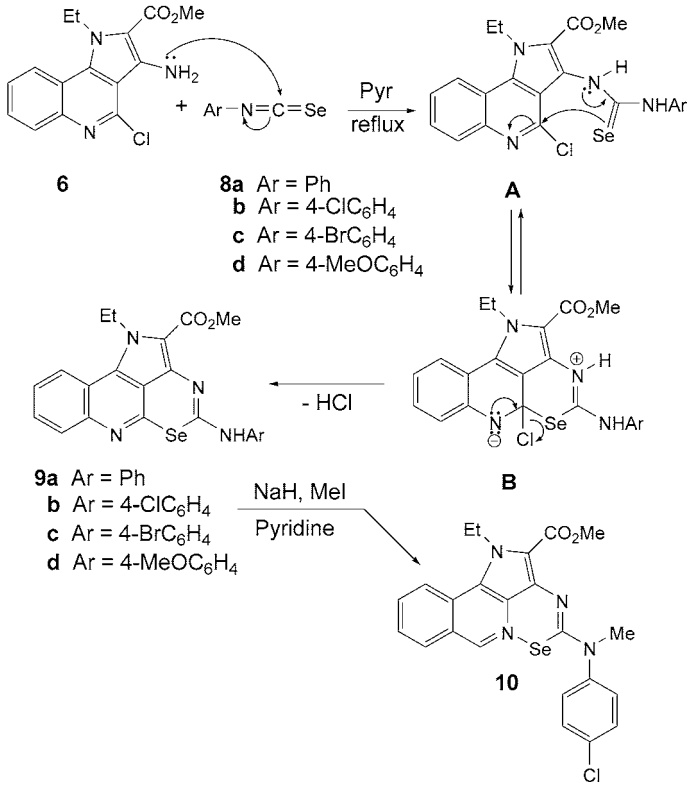


Scheme 2



2. Results and Discussion. – To a solution of **6** in anhydrous pyridine, *ca.* 1.1 equiv. of the freshly prepared aryl isoselenocyanate **8** was added, and the mixture was heated under reflux for 5 h. After evaporation of the solvent, trituration of the residue with MeOH, and recrystallization, the corresponding yellowish crystalline product **9** was obtained (*Scheme 3*). According to the CI-MS and elemental analyses, these products were formed by addition of **6** and **8**, and elimination of HCl. The IR spectra (KBr) showed absorptions at 3274–3244 and 1714–1692 cm^{-1} for NH and the ester C=O group, and the corresponding signals appeared at 10.40–10.06 and 162.8–161.4 ppm in the ^{1}H- and ^{13}C-NMR spectra. Other characteristic signals were present for the EtN

Scheme 3



and the MeO groups as well as for the C-atoms of the polycyclic skeleton in the aromatic region.

As we expected that the formed products were Se analogues of **7** (*Scheme 2*), we tried to form the corresponding diselenides by oxidation (*cf.* [5]), but all attempts failed. Furthermore, methylation of **9b** by treatment with NaH and MeI gave product **10**, which was not a methylseleno derivative. The Me absorption at 3.63 ppm (^{1}H-NMR) clearly shows that **10** is an *N*-Me derivative.

In the case of the 4-bromophenyl derivative **9c**, single crystals were obtained from DMF, and the 1*H*-5-selena-1,3,6-triazaaceanthrylene structure of the molecule was established by X-ray crystallography (*Fig. 1*).

The tetracyclic ring system of **9c** is almost planar, and the ester group is coplanar with the ring system. The 4-bromophenyl ring at N(2) is twisted out of the heterocyclic plane by *ca.* 23° (torsion angles C(2)–N(2)–C(17)–C(18) –158.5(3)°, C(2)–N(2)–C(17)–C(22) 23.9(4)°). The Et group at N(6) is almost orthogonal to the ring skeleton (C(5)–N(6)–C(25)–C(26) –96.5(3)°). The NH group forms an intermolecular H-bond with the O-atom of the ester C=O group of a neighboring molecule, thereby linking the molecules into infinite chains, which run in the [101] direction and have a graph set motif [21] of C(8).

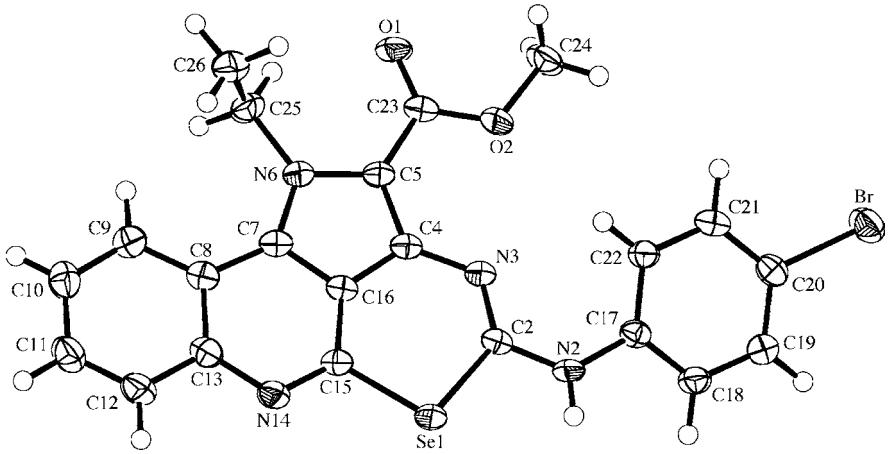
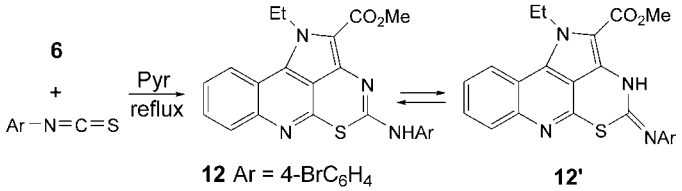


Fig. 1. *ORTEP Plot* [20] *of the molecular structure of* **9c** (arbitrary numbering of atoms; 50% probability ellipsoids)

A reaction mechanism for the formation of **9** is proposed in *Scheme 3*. Nucleophilic addition of the NH_2 group of **6** to the isoselenocyanate **8** leads to the selenoureido derivative **A**. The new selenaheterocycle is formed by nucleophilic substitution of Cl of the 2-chloroquinoline residue *via* attack of the Se-atom, where **B** is an intermediate. As the reaction is carried out in pyridine, a base catalysis of the ring closure is likely.

Because of the discrepancy between the reported reaction of **6** with isothiocyanates (*Scheme 2*) and the reaction with isoselenocyanates (*Scheme 3*), we also carried out a reaction with an aryl isothiocyanate. Treatment of **6** with 4-bromophenyl isothiocyanate in pyridine at room temperature gave **12** in 64% yield (*Scheme 4*). According to the ^{1}H- and ^{13}C-NMR spectra in (D_7)DMF, there are two tautomeric forms **12** and **12′** present in a ratio of *ca.* 2 : 1. Crystals suitable for X-ray crystallography were obtained from DMSO (*Fig. 2*). The molecular structure of **12** is very similar to that of the corresponding Se analogue **9c**. The main difference is that the 4-bromophenyl ring at N(2) is almost coplanar with the heterocyclic ring system (torsion angles C(2)–N(2)–C(17)–C(18) –177.0(2)°, C(2)–N(2)–C(17)–C(22) 2.8(3)°). The asymmetric unit contains one molecule of **12** plus one molecule of DMSO. The NH group forms an intermolecular H-bond with the O-atom of a neighboring DMSO molecule. This interaction does not form an extended network and has a graph set motif of D.

Scheme 4



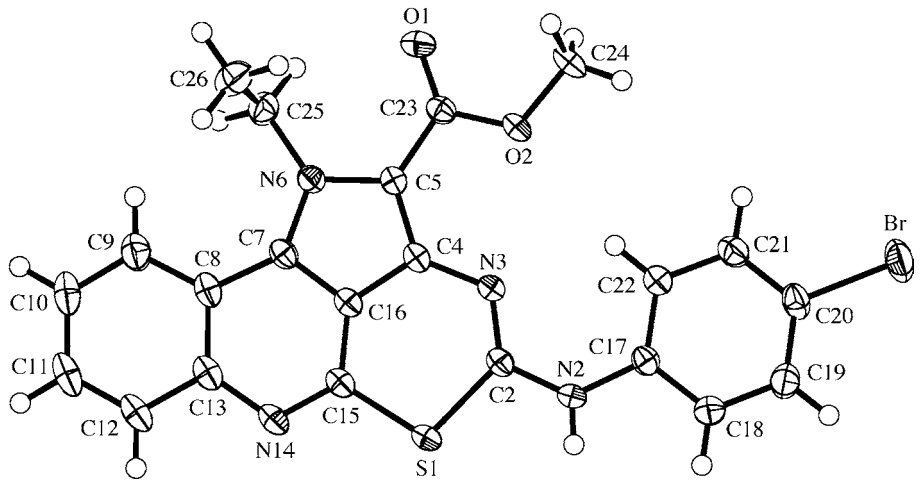
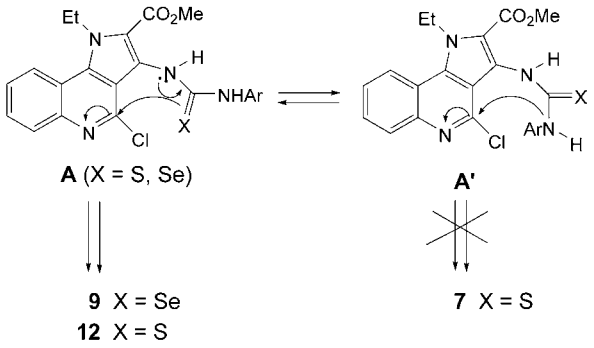


Fig. 2. *ORTEP Plot* [20] *of the molecular structure of* **12** (arbitrary numbering of atoms; 50% probability ellipsoids)

In conclusion, we have shown that the reactions of **6** with aryl isoselenocyanates and isothiocyanates proceed in a consistent manner, leading to the fused tetracyclic ring systems **9** and **12**, respectively. In both cases, the ring closure of the intermediate ureido derivative of type **A** takes place by the nucleophilic attack of the Se- and S-atom (*Scheme 5*). The alternative cyclization *via* the N-atom of the ureido derivatives, which was postulated to lead to the heterocycles of type **7** [19], was not observed. Therefore, the structures proposed in [19] have to be revised.

Scheme 5



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Experimental Part

1. *General*. See [16]. The aryl isoselenocyanates **8a**–**8d** were prepared according to the protocol described in [22]. To a stirred soln. of the corresponding *N*-arylformamide (40 mmol) in abs. toluene (100 ml) in an ice bath were added Et_3N (16.2 g, 160 mmol) and Se black powder. Then, phosgene (30 g of a 20% soln. in toluene, 60 mmol) was added slowly within 30 min. An exothermic reaction took place. After complete addition, the suspension was heated under reflux for 8–10 h (TLC control). The mixture was filtered and washed with several portions of toluene, the filtrate was concentrated and fractionated by column chromatography (SiO_2; hexane). *Phenyl isoselenocyanate* (**8a**) [22]: 4.84 g (40 mmol) of *N*-phenylformamide. Yield: 3.24 g (45%). *4-Chlorophenyl isoselenocyanate* (**8b**) [22]: 6.22 g (40 mmol) of *N*-(4-chlorophenyl)formamide. Yield: 4.77 g (55%). *4-Bromophenyl isoselenocyanate* (**8c**): 8.00 g (40 mmol) of *N*-(4-bromophenyl)formamide. Yield: 6.05 g (58%). *4-Methoxyphenyl isoselenocyanate* (**8d**) [22]: 6.05 g (40 mmol) of *N*-(4-methoxyphenyl)formamide. Yield: 3.56 g (42%). N-*(4-Chlorophenyl)*- and N-*(4-bromophenyl)formamide* were prepared according to [23] by heating the corresponding aniline (20 mmol) in 95% HCOOH under reflux for 30 min. After workup, the products were recrystallized from H_2O. N-*(4-Methoxyphenyl)formamide* was prepared according to [24]. After evaporation of the solvent, the residue was dissolved in AcOEt, and the soln. was washed with 5% aq. $NaHCO_3$ and H_2O. The org. layer was dried ($MgSO_4$), the solvent was evaporated, and the crude product was used without further purification. *Methyl 3-amino-4-chloro-1-ethylpyrrolo[3,2-c]quinoline-2-carboxylate* (**6**) was synthesized according to the protocol in [19]. Cream-colored crystals. M.p. 185–186° (acetone). IR: 3496*m*, 3384*m*, 3068*w*, 3016*w*, 2985*w*, 2956*m*, 2930*w*, 1692*s*, 1602*s*, 1573*s*, 1556*m*, 1534*s*, 1507*s*, 1472*m*, 1435*s*, 1409*w*, 1374*s*, 1356*m*, 1330*m*, 1298*m*, 1276*s*, 1255*m*, 1240*s*, 1180*s*, 1160*s*, 1102*s*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 8.38 (*dd*, J = 8.4, 0.9, 1 arom. H); 7.93 (*dd*, J = 8.2, 1.3, 1 arom. H); 7.73 (*td*, J = 8.2, 1.3, 1 arom. H); 7.67 (*td*, J = 8.4, 1.4, 1 arom. H); 6.04 (*s*, NH_2); 4.84 (*q*, J = 7.0, CH_2); 3.90 (*s*, MeO); 1.47 (*t*, J = 7.0, *Me*CH_2). ^{13}C-NMR ((D_6)DMSO): 161.7 (*s*, CO); 145.1, 144.3, 137.4, 136.4, 116.9, 108.0, 106.8 (7*s*, 7 arom. C); 129.0, 128.8, 126.7, 122.6 (4*d*, 4 arom. CH); 51.1 (*q*, MeO); 42.0 (*t*, CH_2); 15.2 (*q*, *Me*CH_2). CI-MS: 304 (100, $[M+1]^+$). Anal. calc. for $C_{15}H_{14}ClN_3O_2$ (303.74): C 59.31, H 4.65, N 13.83; found C 59.15, H 4.63, N 13.84.

2. *Preparation of 1*H-*5-Selena-1,3,6-triazaaceanthrylene-2-carboxylates* **9a**–**9d**. *General Procedure.* To a soln. of **6** in anh. pyridine, the freshly prepared aryl isoselenocyanate **8** was added under stirring at r.t. The mixture was heated under reflux for 5 h. After cooling, the solvent was evaporated *i.v.*, and the remaining oily residue was triturated with MeOH. The resulting solid product was collected by filtration and purified by recrystallization from MeOH or CH_2Cl_2/hexane.

*Methyl 1-Ethyl-4-(phenylamino)-1*H-*5-selena-1,3,6-triazaaceanthrylene-2-carboxylate* (**9a**). From 0.5 g (1.64 mmol) of **6** and 0.33 g (1.81 mmol) of **8a**. Yield: 0.55 g (75.3%). Yellowish crystals. M.p. 256.1–257.0° (MeOH). IR: 3244*w*, 3191*w*, 3125*w*, 3047*m*, 3012*m*, 2974*m*, 2931*m*, 1714*s*, 1628*s*, 1590*s*, 1569*s*, 1557*s*, 1546*s*, 1496*s*, 1456*m*, 1438*s*, 1371*m*, 1354*m*, 1312*m*, 1295*m*, 1269*m*, 1244*m*, 1216*m*, 1199*m*, 1183*m*, 1163*m*, 1140*w*, 1111*s*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 10.20 (*s*, NH); 8.33 (*d*, J = 7.6, 1 arom. H); 8.09 (*d*, J = 8.0, 2 arom. H); 7.91 (*dd*, J = 8.2, 1.2, 1 arom. H); 7.68 (*td*, J = 8.1, 1.1, 1 arom. H); 7.61 (*td*, J = 8.3, 1.3, 1 arom. H); 7.39 (*dd*, J = 8.4, 7.4, 2 arom. H); 7.08 (*t*, J = 7.3, 1 arom. H); 4.95 (*q*, J = 7.0, CH_2); 3.99 (*s*, MeO); 1.51 (*t*, J = 7.0, *Me*CH_2). ^{13}C-NMR ((D_6)DMSO): 161.4 (*s*, CO); 152.4, 147.6, 147.2, 140.4, 135.4, 131.1 (6*s*, 7 arom. C); 128.7, 128.6, 128.5, 125.9, 122.9, 122.5, 119.4 (7*d*, 9 arom. CH); 117.9, 105.0 (2*s*, 2 arom. C); 51.5 (*q*, MeO); 41.9 (*t*, CH_2); 15.4 (*q*, *Me*CH_2). CI-MS: 451 (100, $[M+1]^+$). Anal. calc. for $C_{22}H_{18}N_4O_2Se$ (449.36)[2]): C 58.80, H 4.04, N 12.47; found: C 56.84, H 4.25, N 11.95.

*Methyl 4-[(4-Chlorophenyl)amino]-1-ethyl-1*H-*5-selena-1,3,6-triazaaceanthrylene-2-carboxylate* (**9b**). From 0.4 g (1.31 mmol) of **6** and 0.31 g (1.42 mmol) of **8b**. Yield: 0.55 g (87.3%). Yellowish crystals. M.p. 271.0–272.1° (MeOH). IR: 3261*w*, 3190*w*, 3102*m*, 3055*m*, 2990*m*, 2950*m*, 1694*s*, 1605*s*, 1570*s*, 1549*s*, 1489*s*, 1461*m*, 1435*s*, 1420*w*, 1400*m*, 1373*s*, 1353*m*, 1308*s*, 1292*s*, 1263*m*, 1246*m*, 1223*s*, 1196*m*, 1180*m*, 1161*m*, 1135*w*, 1110*s*, 1094*m*. ^{1}H-NMR ((D_7)DMF): 10.62 (*s*, NH); 8.62 (*d*, J = 8.2, 1 arom. H); 8.50 (*d*, J = 8.8, 2 arom. H); 8.18 (*d*, J = 8.0, 1 arom. H); 7.95–7.82 (*m*, 2 arom. H); 7.71 (*d*, J = 8.8, 2 arom. H); 5.26 (*q*, J = 7.0, CH_2); 4.35 (*s*, MeO); 1.85 (*t*, J = 7.0, *Me*CH_2). ^{13}C-NMR ((D_7)DMF): 162.8 (*s*, CO)[3]); 153.0, 148.5, 140.5, 132.0, 129.8, 129.3, 118.1 (7*s*, 10 arom. C); 129.1, 127.5, 126.5, 123.4, 121.5, 119.0 (6*d*, 8 arom. CH); 52.2 (*q*, MeO); 42.9 (*t*, CH_2); 15.9 (*q*, *Me*CH_2). CI-MS: 485 (100, $[M+1]^+$). Anal. calc. for $C_{22}H_{17}ClN_4O_2Se$ (483.81): C 54.62, H 3.54, N 11.58; found: C 53.88, H 3.65, N 11.41.

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[2]) In all Se-containing products, the values for C were too low.

[3]) Signal overlaps with the signal of DMF.

*Methyl 4-[(4-Bromophenyl)amino]-1-ethyl-1*H*-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate* (**9c**). From 0.6 g (1.97 mmol) of **6** and 0.56 g (2.14 mmol) of **8c**. Yield: 0.9 g (86.5%). Colorless crystals. M.p. 265–267° (MeOH), 266.8–267.0° (CH_2Cl_2/hexane). IR: 3274*m*, 3186*m*, 3099*m*, 3050*m*, 2989*m*, 1694*s*, 1606*s*, 1586*s*, 1570*s*, 1546*s*, 1487*s*, 1461*m*, 1435*m*, 1395*m*, 1374*m*, 1354*w*, 1309*s*, 1294*s*, 1264*m*, 1246*m*, 1223*s*, 1197*m*, 1181*m*, 1160*m*, 1135*w*, 1111*m*. ^{1}H-NMR ((D_7)DMF): 10.40 (*s*, NH); 8.40 (*d*, $J = 8.1$, 1 arom. H); 8.21 (*d*, $J = 8.5$, 2 arom. H); 7.94 (*d*, $J = 8.1$, 1 arom. H); 7.69 (*t*-like, 2 arom. H); 7.61 (*d*-like, 2 arom. H); 5.03 (*q*, $J = 7.0$, CH_2); 4.11 (*s*, MeO); 1.60 (*t*, $J = 7.0$, *Me*CH_2). ^{13}C-NMR ((D_7)DMF): 162.7 (*s*, CO)[3]); 153.1, 148.6, 148.5, 140.9, 136.0, 131.2, 119.0, 117.6, 115.2, 105.8 (10*s*, 10 arom. C); 132.3, 129.9, 129.1, 126.5, 123.4, 121.9 (6*d*, 8 arom. CH); 52.2 (*q*, MeO); 42.9 (*t*, CH_2); 15.9 (*q*, *Me*CH_2). CI-MS: 529 (100, $[M+1]^+$). Anal. calc. for $C_{22}H_{17}BrN_4O_2Se$ (528.26): C 50.02, H 3.24, N 10.61; found C 49.33, H 3.43, N 10.50.

*Methyl 1-Ethyl-4-[(4-methoxyphenyl)amino]-1*H*-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate* (**9d**). From 0.4 g (1.31 mmol) of **6** and 0.36 g (1.69 mmol) of **8d**. Yield: 0.5 g (79.4%). Yellowish crystals. M.p. 249.2–250.0° (CH_2Cl_2/hexane). IR: 3262*w*, 3198*w*, 3123*w*, 3062*m*, 2988*m*, 2949*m*, 2833*w*, 1692*s*, 1601*s*, 1569*s*, 1535*m*, 1508*s*, 1476*m*, 1460*m*, 1438*m*, 1414*m*, 1372*m*, 1354*m*, 1297*m*, 1279*w*, 1241*s*, 1218*s*, 1197*m*, 1179*w*, 1161*m*, 1136*w*, 1110*m*. ^{1}H-NMR (500 MHz, (D_6)DMSO): 10.06 (*s*, NH); 8.30 (br. *d*, $J = 8.0$, 1 arom. H); 8.00 (br. *d*, $J = 8.8$, 2 arom. H); 7.89 (*dd*, $J = 8.2$, 1.2, 1 arom. H); 7.66 (*td*, $J = 8.2$, 1.2, 1 arom. H); 7.58 (*td*, $J = 8.2$, 1.2, 1 arom. H); 6.94 (*d*-like, $J = 9.1$, 2 arom. H); 4.93 (*q*, $J = 7.0$, CH_2); 3.97, 3.77 (2*s*, 2 MeO); 1.50 (*t*, $J = 7.0$, *Me*CH_2). ^{13}C-NMR ((D_6)DMSO): 161.3 (*s*, CO); 154.9, 152.4, 147.1, 135.6, 133.7, 131.0, 128.4, 115.9, 104.6 (9*s*, 10 arom. C); 128.5, 125.8, 122.5, 120.5, 117.7, 113.7 (6*d*, 8 arom. CH); 55.2, 51.6 (2*q*, 2 MeO); 41.8 (*t*, CH_2); 15.3 (*q*, *Me*CH_2). CI-MS: 481 (100, $[M+1]^+$). Anal. calc. for $C_{23}H_{20}N_4O_3Se$ (479.39): C 57.62, H 4.21, N 11.69; found C 55.90, H 4.22, N 11.32.

*Methyl 4-[(4-Chlorophenyl)(methyl)amino]-1-ethyl-1*H*-5-selena-1,3,6-triazaaceanthrylene-2-carboxylate* (**10**). To a soln. of **9b** (0.2 g, 0.4 mmol) in dry pyridine (30 ml) was added a suspension of NaH in mineral oil (*ca*. 1.5 equiv.) and 1.2 equiv. MeI. Usual workup and crystallization yielded 0.1 g (50%) of **10**. Creamy-colored crystals. M.p. 215.1–215.5° (CH_2Cl_2/hexane). IR: 3181*w*, 3048*w*, 2927*m*, 1695*s*, 1611*m*, 1596*s*, 1584*s*, 1567*s*, 1552*s*, 1489*s*, 1461*s*, 1435*s*, 1405*m*, 1373*s*, 1350*m*, 1314*s*, 1285*s*, 1263*m*, 1243*m*, 1222*s*, 1191*s*, 1158*m*, 1127*m*, 1110*s*, 1090*m*. ^{1}H-NMR ((D_7)DMF): 8.37 (*d*, $J = 8.3$, 1 arom. H); 8.35 (*d*-like, 1 arom. H); 7.88 (*d*-like, 2 arom. H); 7.85–7.49 (*m*, 4 arom. H); 5.00 (*q*, $J = 6.8$, CH_2); 3.97 (*s*, MeO); 3.63 (*s*, MeN); 1.57 (*t*, $J = 7.0$, $MeCH_2$). CI-MS: 499 (100, $[M+1]^+$).

3. *Preparation of Methyl 4-[(4-Bromophenyl)amino]-1-ethyl-1*H*-5-thia-1,3,6-triazaaceanthrylene-4-carboxylate* (**12**). In analogy to the *General Procedure* (*Sect. 2*), **12** was prepared from 0.4 g (1.32 mmol) of **6** and 0.29 g (1.35 mmol) of 4-bromophenyl isothiocyanate. Yield: 0.4 g (63.5%). Pale-yellow crystals. M.p. 286.1–286.5° (MeOH). IR: 3416*w*, 3305*s*, 3194*m*, 3120*m*, 3054*w*, 2946*w*, 2926*w*, 2852*w*, 1662*s*, 1601*s*, 1562*s*, 1540*s*, 1487*s*, 1468*s*, 1439*m*, 1395*m*, 1378*m*, 1353*w*, 1308*s*, 1293*m*, 1261*m*, 1249*w*, 1223*s*, 1199*m*, 1179*m*, 1157*m*, 1132*m*, 1116*m*. ^{1}H-NMR ((D_7)DMF)[4]): 12.93 (*s*, 0.33 NH); 10.43 (*s*, 0.66 NH); 8.61–8.59 (*d*-like, 0.33 arom. H); 8.39–8.37 (*d*-like, 0.66 arom. H); 8.24–8.22 (*m*, 2 arom. H); 7.93–7.92 (*d*-like, 0.33 arom. H); 7.89–7.88 (*d*-like, 0.66 arom. H); 7.70–7.53 (*m*, 4 arom. H); 5.04 (*q*, $J = 7$, CH_2); 4.09, 4.04 (2*s*, MeO); 1.59 (*t*, $J = 7$, *Me*CH_2). ^{13}C-NMR ((D_7)DMF)[4]): 162.4, 162.0 (2*s*, CO); 153.0, 151.6, 151.1, 148.5, 148.0, 140.8, 135.1, 132.8, 132.6, 119.2, 119.1, 116.1, 115.3, 107.1, 10.2 (15*s*, 10 arom. C); 132.3, 132.2, 129.9, 129.4, 129.2, 126.5, 126.2, 123.6, 123.4, 122.3, 122.2 (11*d*, 8 arom. CH); 52.0, 51.9 (2*q*, MeO); 42.8 (*t*, CH_2); 15.9 (*q*, *Me*CH_2). CI-MS: 483 (100, $[M+1]^+$). Anal. calc. for $C_{22}H_{17}BrN_4O_2S$ (481.36): C 54.89, H 3.56, N 11.64; found: C 54.06, H 3.68, N 11.54.

4. *X-Ray Crystal-Structure Determination of* **9c** *and* **12** (*Table*, and *Figs. 1* and *2*)[5]). All measurements were performed on a *Nonius KappaCCD* diffractometer [25] with graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream*-700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1* and *2*. Data reductions were performed with *HKL Denzo* and *Scalepack* [26]. The intensities were corrected for *Lorentz* and polarization effects, and, in the case of **9c**, a numerical absorption correction [27] was applied, whereas, in the case of **12**, an absorption correction based on the multi-scan method [28] was applied. The structures were solved by direct methods using SIR92 [29], which revealed the positions of all non-H-atoms. In the case of **12**, the asymmetric unit contains one

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[4]) Two tautomeric forms of **12** are present in a ratio of *ca*. 1:2. Some of the signals overlap.

[5]) CCDC-211324 and 211325 contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223–336033; e-mail: deposit@ccdc.cam.ac.uk)).

Table. *Crystallographic Data of Compounds* **9c** *and* **12**

	9c	**12**
Crystallized from	DMF	DMSO
Empirical formula	$C_{22}H_{17}BrN_4O_2Se$	$C_{22}H_{17}BrN_4O_2S \cdot C_2H_6OS$
Formula weight	528.21	559.49
Crystal color, habit	colorless, plate	pale yellow, plate
Crystal dimensions [mm]	$0.05 \times 0.20 \times 0.23$	$0.05 \times 0.15 \times 0.22$
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
Reflections for cell determination	67221	41355
2θ Range for cell determination [°]	4–55	4–60
Unit cell parameters a [Å]	13.0270(3)	11.5740(1)
b [Å]	9.4013(3)	9.1938(1)
c [Å]	17.5241(5)	22.3318(3)
β [°]	110.975(1)	92.7150(5)
V [Å^3]	2004.0(1)	2373.64(5)
D_x [g cm^{-3}]	1.751	1.565
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	3.901	1.948
Transmission factors [min; max]	0.463; 0.852	0.728; 0.930
Scan type	ϕ and ω	ϕ and ω
$2\theta_{(\max)}$ [°]	55	60
Total reflections measured	42812	58214
Symmetry-independent reflections	4560	6912
Reflections with $I > 2\sigma(I)$	3347	4925
Reflections used in refinement	4560	6912
Parameters refined	278	316
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0369	0.0382
$wR(F^2)$ (all data)	0.0851	0.0960
Weighting parameters [a; b][a])	0.0340; 1.4557	0.0434; 0.5372
Goodness-of-fit	1.058	1.038
Secondary extinction coefficient	0.0021(3)	0.0037(6)
Final $\Delta_{\max}/\sigma$	0.001	0.005
$\Delta\rho$ (max; min) [e Å^{-3}]	0.66; −0.56	0.50; −0.41

[a]) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$.

molecule of **12** plus one molecule of DMSO. The non-H-atoms were refined anisotropically. In both structures, the NH-atom was placed in the position indicated by a difference-electron-density map, and its position was allowed to refine together with an isotropic displacement parameter. All remaining H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). Refinements of the structures were carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in both cases. Neutral atom scattering factors for non-H-atoms were taken from [30a], and the scattering factors for H-atoms were taken from [31]. Anomalous dispersion effects were included in F_c [32]; the values for f' and f'' were those of [30b]. The values of the mass attenuation coefficients are those of [30c]. All calculations were performed using the SHELXL97 program [33].

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